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Variational calculations on the hydrogen molecular ion

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Abstract

We present high-precision non-relativistic variational calculations of bound vibrational-rotational state energies for the H_2^+ and D_2^+ molecular ions in each of the lowest electronic states of Σ_g, Σ_u, and Π_u symmetry. The calculations are carried out including coupling between Σ and Π states but without using the Born-Oppenheimer or any adiabatic approximation. Convergence studies are presented which indicate that the resulting energies for low-lying levels are accurate to about 10^{-13}. Our procedure accounts naturally for the lambda-doubling of the Π_u state.

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I. INTRODUCTION

There are many calculations of bound state energies of the hydrogen molecular ion H_2^+ using the Born-Oppenheimer approximation or various adiabatic approximations and there are a number of studies that investigate deviations of energies from the Born-Oppenheimer values. The present work is a systematic high precision nonadiabatic[1] study of H_2^+ and D_2^+ in each of the lowest electronic states of Σ_g, Σ_u, and Π_u symmetry carried out using variational basis sets. It is motivated by recent precise experimental spectroscopy of Rydberg states of the hydrogen and deuterium molecules that has led to accurate experimental values of the the electric dipole polarizability of the corresponding molecular ions in their ground states [1]. These experiments were followed by several papers detailing various nonadiabatic calculations of the electric dipole polarizability [2–5]. The present paper is the first in a series. We are using the eigenstates studied in the present work in a study of the electric dipole sum rules for H_2^+ and D_2^+, including the polarizability.

Several investigators have performed nonadiabatic calculations on the ground electronic state of H_2^+ since Hunter and Pritchard [6] and Kołos [7] reported the first precision calculations. The most accurate calculations used variational basis set methods [8,9], variation-perturbation methods [10,11], and artificial channel scattering methods [12,13]. Variational basis set calculations can be in principle quite accurate but appear to have been applied only to the lowest-lying eigenvalues of the Σ_g symmetry. The variation-perturbation and the artificial channel methods yield energies for all of the vibration-rotational levels and have been applied to the states of Σ_g and Σ_u symmetry. There are other approaches applied to the Σ_g symmetry that have not yet reported precision as great as those mentioned above such as the adaptive finite element method [14], the generator coordinate method [15], quantum Monte Carlo [16] and perturbative approaches [17]. Energy calculations up to 1980 were reviewed by Bishop and Cheung [18] and a useful, more general review covering up to 1995 can be found in [19].

II. THEORY

In this section we derive the Hamiltonian and introduce the basis sets we used. Other derivations can be found in Refs. [20–23,10,24]. Some of the operators we use were introduced in those references and Ref. [25]. Our intention is to avoid writing explicit matrix elements until the last steps and the spirit of the present derivation is closest to the derivations in Refs. [20,22,26].

A. Hamiltonian

In a space-fixed frame and with the center of mass motion removed the Hamiltonian for the homonuclear one-electron diatomic molecule is

[1]We would prefer to use the term 'batic, which we coined to avoid the double negative implied in nonadiabatic, but clarity must yield to convention.

$$H = -\tfrac{1}{2}M^{-1}\nabla_R^2 - [\tfrac{1}{2} + \tfrac{1}{8}M^{-1}]\nabla^2 + V(\mathbf{r},\mathbf{R}), \tag{1}$$

where

$$V(\mathbf{r},\mathbf{R}) = -\frac{1}{|\mathbf{r} - \frac{1}{2}\mathbf{R}|} - \frac{1}{|\mathbf{r} + \frac{1}{2}\mathbf{R}|} + \frac{1}{R} \tag{2}$$

and $M = \frac{1}{2}M_n$, with M_n the nuclear mass, $\mathbf{r}$ the position vector of the electron from the midpoint of the vector $\mathbf{R}$ joining the nuclei, and $R = |\mathbf{R}|$. We use atomic units throughout. The electronic (cartesian) coordinates are to be held fixed in the space-fixed frame in carrying out the derivatives in the gradient operator ∇_R appearing in Eq. (1) [27,28].

Following Ref. [29] we introduce the rotational angular momentum $\mathcal{R}$ implicitly expressing the Hamiltonian in a rotating molecular fixed frame. The nuclear kinetic energy is written as

$$-\frac{\nabla_R^2}{2M} = \frac{1}{2MR^2}\left(-\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \mathcal{R}^2\right). \tag{3}$$

Defining a rotational Hamiltonian

$$H_{\rm rot} = \frac{\mathcal{R}^2}{2MR^2} \tag{4}$$

we write

$$-\frac{\nabla_R^2}{2M} = -\frac{1}{2MR^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + H_{\rm rot}, \tag{5}$$

where the three spherical polar coordinates comprised of R and the two angles (contained in the $\mathcal{R}^2$ operator of $H_{\rm rot}$) contain the information on the orientation of the molecular fixed frame with respect to the space fixed frame.

Since here we are ignoring electron and nuclear spins, the total angular momentum is $\mathbf{N} = \mathcal{R} + \mathbf{L}$, where $\mathbf{L}$ is the electronic angular momentum. Using $\mathcal{R} = \mathbf{N} - \mathbf{L}$, we replace $\mathcal{R}^2$ in Eq. (4) giving

$$H_{\rm rot} = \frac{1}{2MR^2}(\mathbf{N} - \mathbf{L})^2 = \frac{1}{2MR^2}(N^2 + L^2 - N^-L^+ - N^+L^- - 2N_zL_z), \tag{6}$$

where the superscripts on L^+ and L^- and subscript z on L_z refer to the components in the molecule-fixed frame [29].

Changing the electron coordinates from cartesian to prolate spheroidal coordinates (λ,μ,χ), we have $r = |\mathbf{r}| = \frac{R}{2}(\lambda^2 + \mu^2 - 1)^{1/2}$. The operator $\frac{\partial}{\partial R}$ in (3) is taken with the electronic (prolate spheroidal) coordinates held fixed in the molecular fixed frame and can be expressed as

$$\frac{\partial}{\partial R} = \frac{\partial}{\partial R}\,)_{\lambda,\mu} - \frac{\partial r}{\partial R}\frac{\partial}{\partial r}, \tag{7}$$

where the term $\frac{\partial}{\partial R}$ on the LHS of Eq. (7) refers to the derivative with the electronic (cartesian) coordinates held fixed as in Eq. (3).

Using the RHS of Eq. (7) in Eq. (3) we can write the kinetic energy operator as

$$-\frac{\nabla_R^2}{2M} = \frac{1}{2M}\left[-\frac{\partial^2}{\partial R^2} - \frac{2}{R}\frac{\partial}{\partial R} + \frac{2Y}{R^2}\frac{\partial}{\partial R}R - \frac{r^2}{R^2}p_r^2 + H_{\rm rot}\right], \tag{8}$$

where

$$p_r^2 = -\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} \tag{9}$$

and

$$Y = r\frac{\partial}{\partial r} \tag{10}$$

and it is now understood that the electronic (prolate spheroidal) coordinates are held fixed where appropriate.

We use the expression

$$-p_r^2 - \frac{L^2}{r^2} = \nabla^2 \tag{11}$$

to combine Eq. (8) and (6), yielding

$$-\frac{\nabla_R^2}{2M} = \frac{1}{2M}\left[-\frac{\partial^2}{\partial R^2} - \frac{2}{R}\frac{\partial}{\partial R} + \frac{2Y}{R^2}\frac{\partial}{\partial R}R + \frac{r^2}{R^2}\nabla^2 + \frac{1}{R^2}(N^2 - N^-L^+ - N^+L^- - 2N_zL_z)\right]. \tag{12}$$

We define for later use the coupling term

$$\frac{1}{2MR^2}(-N^-L^+ - N^+L^-) \tag{13}$$

that enters from Eq. (12) into the Hamiltonian.

The potential energy is given in terms of the prolate spheroidal coordinate system (λ, μ, χ) by

$$V(\lambda, \mu, R) = \frac{1}{R} - \frac{4\lambda}{R(\lambda^2 - \mu^2)}, \tag{14}$$

and the electronic kinetic energy operator by

$$\nabla^2 = (4/R^2)[X + (\lambda^2 - 1)^{-1}(1 - \mu^2)^{-1}\partial^2/\partial\chi^2], \tag{15}$$

where

$$X = (\lambda^2 - \mu^2)^{-1}[(\partial/\partial\lambda)(\lambda^2 - 1)\partial/\partial\lambda + (\partial/\partial\mu)(1 - \mu^2)\partial/\partial\mu]. \tag{16}$$

and the operator Y, Eq. (10), becomes

$$Y = (\lambda^2 - \mu^2)^{-1}[\lambda(\lambda^2 - 1)\partial/\partial\lambda + \mu(1 - \mu^2)\partial/\partial\mu]. \tag{17}$$

The terms in $\mathbf{L}$ can be reexpressed in the (λ, μ, χ) coordinates, see for example Ref. [30].

The remainder of the Hamiltonian derivation follows that of, for example [10], and in this way the Hamiltonian reduces to effective matrix elements that may be evaluated as integrals over λ, μ, and χ.

B. Basis sets and trial functions

For the electronic states of Σ_g, Σ_u and Π_u symmetry investigated here we used a basis set composed of functions of the form [24]

$$\Phi_{bc}^{\Lambda p}(\lambda,\mu,\chi) = (\lambda^2-1)^{|\Lambda|/2} L_b^{|\Lambda|}[\alpha(\lambda-1)] \exp[-\tfrac{1}{2}\alpha(\lambda-1)] P_c^{|\Lambda|}(\mu) \exp(i\Lambda\chi), \tag{18}$$

with $b = 0, ..., B$ and α a nonlinear parameter. We used values of $\Lambda = -1, 0$, and 1. The values $|\Lambda| = 0$ and 1 correspond, respectively, to Σ and Π states. For the Σ_g symmetry $c = 0, 2, .., 2C$ and $p = g$, for the Σ_u and Π_u symmetries $c = 1, 3, ..., 2C+1$ and $p = u$, and for the Π_g symmetry $c = 2, 4, ..., 2C+2$ with $p = g$.

The trial function for a particular set of states specified by Λ, p, and N has the form

$$\Psi_{\Lambda pN}(\lambda,\mu,\chi,R) = \sum_{s[bcd]=1}^{S} k_{s[bcd]} \Phi_{bc}^{\Lambda p}(\lambda,\mu,\chi)\chi_d(R) \tag{19}$$

where $\Phi_{bc}^{\Lambda p}$ is given in Eq. (18) and where $S = (B+1)(C+1)(D+1)$. The index $s \equiv [bcd]$ was filled in the order $[\{b,\{c,\{d\}\}\}]$, where $\{b\}$, for example, indicates a loop over all possible values of the index $b = 0, ..., B$. The vibrational basis functions were of the form

$$\chi_d(R) = (1/R)(\gamma R)^{(\beta+1)/2} L_d^{\beta}(\gamma R) \exp(-\tfrac{1}{2}\gamma R), \tag{20}$$

with $d = 0, ..., D$. The vibrational state quantum numbers were identified with levels in the spectrum resulting from the diagonalization. The eigenvalues approach the exact eigenenergies behaving as expected by the Hylleraas-Undheim theorem [31].

Laguerre polynomials were used in the electronic basis because the integrals involved could be solved in closed form. Other possibilities explored such as Hermite polynomials did not offer this advantage. The electronic basis (18) is independent of R and is identical to that used by Moss and Sadler [24]. The vibrational basis is similar to theirs in functional form, but we used a different nonlinear parameter γ that allowed us to avoid certain expressions involving hypergeometric series and thereby offered an apparent improvement in speed. We expect that the accuracy of our vibrational basis is at least equal to that of Moss and Sadler.

III. CALCULATION

Matrix elements of the Hamiltonian over the basis set functions and the overlap between basis set functions were set up as four-dimensional integrals over λ, μ, χ, and R. The evaluations reduce to integrals over λ, μ, and R. The eigenvalues were obtained using the Rayleigh-Ritz method by solution of the generalized eigenvalue problem for the Hamiltonian and overlap matrices and iteratively varying the nonlinear parameters. Some details on the integrals and procedures are presented in this section.

A. Evaluation of the integrals

Consider the integrals over λ and over R required for evaluation of the Hamiltonian and overlap matrix elements. Any integrals containing derivatives were manipulated to eliminate the derivatives by utilizing

$$\frac{\partial}{\partial x} L_n^a(x) = -L_{n-1}^{a+1}(x) \tag{21}$$

and

$$L_n^a(x) = \sum_{k=0}^{n} L_k^{a-1}(x) \tag{22}$$

to rewrite each integrand as a linear combination of integrals of the form

$$\int_0^\infty dx\, x^{a+r} L_m^a(x) L_n^a(x) e^{-x}, \tag{23}$$

where r is an integer, $r \geq 0$.

The resulting sets of integrals of form (23), and any other integrals of that form, were then manipulated to eliminate the powers of λ. This was done by writing the product $x^r L_m^a(x)$ as a linear combination of Laguerre polynomials with the same superscript. To this end, the expression

$$x L_n^a(x) = (n+a) L_n^{a-1}(x) - (n+1) L_{n+1}^{a-1}(x), \tag{24}$$

derived using the summation definition for associated Laguerre polynomials, can be reduced using

$$L_n^a(x) = L_n^{a+1}(x) - L_{n-1}^{a+1}(x) \tag{25}$$

to the desired expression,

$$x L_n^a(x) = (2n+a+1) L_n^a(x) - (n+1) L_{n+1}^a(x) - (n+a) L_{n-1}^a(x). \tag{26}$$

Substituting Eq. (26) into Eq. (23), each integral over λ can now be expressed as a sum of integrals of the form

$$\int_0^\infty dx\, x^a L_m^a(x) L_n^a(x) e^{-x} = \delta_{mn} (m+a)!/m!. \tag{27}$$

The integrals involving μ could be performed through simple manipulations of associated Legendre polynomials.

Coupling between states of different Λ introduced two problems. The first was that in order to carry out manipulations such as those used above leading to (27), we required expressions for raising or lowering superscripts by more than unity. Using Eq. (22) we derived the relation

$$L_n^a(x) = \sum_{k=0}^{n} \binom{l+k-1}{k} L_{n-k}^{a-l}(x) \tag{28}$$

and similarly from repeated application of Eq. (25) we derived the relation

$$L_n^a(x) = \sum_{k=0}^{l} (-1)^k \binom{l}{k} L_{n-k}^{a+l}(x). \tag{29}$$

The second problem was the coupling of different γ parameters. By using the same manipulations as for the λ integral, we reduce the vibrational integral to a linear combination of functions I, where

$$I(a,m,n,\gamma_i,\gamma_j) \equiv \int_0^\infty dx\, x^a L_m^a(\gamma_i x) L_n^a(\gamma_j x) \exp(-\tfrac{1}{2}(\gamma_i+\gamma_j)x), \tag{30}$$

which can be reexpressed in terms of the hypergeometric function ${}_2F_1$ using Eq. (7.414.4) of Ref. [32] as

$$I(a,m,n,\gamma_i,\gamma_j) = F(-m,-n;-m-n-a;\gamma_{\rm rat}^2)\frac{(m+n+a)!}{m!n!}2^{a+1}(-1)^m\gamma_{\rm rat}^{-n-m}(\gamma_i+\gamma_j)^{-a-1}, \tag{31}$$

where

$$\gamma_{\rm rat} \equiv (\gamma_i+\gamma_j)/(\gamma_i-\gamma_j). \tag{32}$$

The hypergeometric series terminates since $m \geq 0$ and $n \geq 0$. Some additional notes on evaluating integrals of Laguerre and Legendre polynomials are given in [24]. Maple V was used to check the evaluation of the matrix elements and it was used to output them into Fortran code.

B. Numerical procedures

The trial functions (19) have three sectors. They are comprised of two electronic sectors, labeled by the indices b and c and governed by the nonlinear parameter α, and one vibrational sector, labeled by the index d and governed by the nonlinear parameters β and γ. In our calculations each sector was treated separately in optimizing the nonlinear parameters and in studying convergence as the basis size was increased. The eigenvalues and wave functions were determined by solution of the secular equation using the LAPACK routines DSYGV and DSPGV, part of the math subroutine library DXML. The energy was further minimized by iteratively varying various nonlinear parameters (using a procedure discussed below) and rediagonalizing. For small basis set sizes we used a conjugate gradient method and then minimized by hand and for the larger basis set sizes we used an algorithm similar to Brent's [33]. Minimization of α was accomplished with standard algorithms. The optimum values for the parameters β and γ were more difficult to determine for two reasons. First, β is integer and the necessarily discrete choices impeded the optimization; furthermore, a change in β does not correspond to a parabolic change in the value of the energy. Second, the nonlinear parameters β and γ are intrinsically linked requiring simultaneous minimization.

A general procedure was developed which allowed us to optimize α, β, and γ efficiently. Four steps can be identified. 1) We fixed β and γ and then α was optimized for a minimum energy. 2) To minimize on β and γ we fixed β and then minimized on γ. The parameter β was then varied by a large interval (about 6) and then we minimized again on γ. Some care was required in selecting what would be the optimum values of γ as false local minima occasionally appeared. 3) Values of β within the final interval were searched for the optimum value with minimization on γ. 4) After all of the above α was reoptimized with the selected

β and γ. In all cases it was found in step 4) that the value of α was the same as that found in step 1), an important verification of our choice of final optimized nonlinear parameters.

Having fixed the nonlinear parameters the basis set size was systematically increased to obtain precise eigenvalues by expanding each sector separately. Convergence to the final value was logarithmic. For $H_2{}^+$ in Figs. 1, 2, and 3 the convergence is demonstrated by plotting the difference between the energy for a particular basis set dimension and the energy for a basis set of dimension one unit larger. Results for $D_2{}^+$ are similar. For each figure, we begin with the final optimized wave function. The nonlinear parameters are not changed but the basis set dimension is set to $B = 2$, then index B is increased with the others held fixed at their optimized values and the difference between successive energies is plotted yielding the curves labeled "B (Electronic)" and similarly for C and D. For the Σ_u states of $H_2{}^+$ and $D_2{}^+$ convergence in the vibrational sector is slower than for the Σ_g and Π_u states so we extrapolated to the desired numerical accuracy using linear regression on the log of the energy differences. Figure 2 illustrates the slow convergence but also the validity of the extrapolation. The basis set dimensions and nonlinear parameters for states with $N = 0$ are given in Table I for Σ_g symmetry in the first row under "Type I" and for Σ_u symmetry in the first row under "Type II".

For the states with $N > 0$, the off-diagonal term Eq. (13) in the Hamiltonian requires the inclusion of coupling between basis sets of Σ and Π symmetry. Denoting the electronic basis sets by their value of Λ as $|\Lambda\rangle$ we set up matrix elements of the Hamiltonian using the rotated basis $\frac{1}{\sqrt{2}}(|+1\rangle + |-1\rangle)$ and $\frac{1}{\sqrt{2}}(|+1\rangle - |-1\rangle)$. With it there is only coupling between $|0\rangle$ and $\frac{1}{\sqrt{2}}(|+1\rangle - |-1\rangle)$. A two by two matrix of matrices was created with the uncoupled Hamiltonian matrix elements for each basis set as the diagonal elements and the matrix elements of the coupling term Eq. (13) between the two basis sets as the off-diagonal elements. The energies of the states were determined by diagonalization of this matrix, while the energies corresponding to the uncoupled basis $\frac{1}{\sqrt{2}}(|+1\rangle + |-1\rangle)$ were determined by diagonalization of the uncoupled Hamiltonian. For each state, the non-linear parameters and basis size were fixed at the values already determined for the minimum energies. Then the same technique used for the uncoupled energies was applied to the coupled basis sets to determine non-linear parameters and basis sizes that minimized the energy of the state under consideration. For example, when trying to determine the $\Sigma_u, v = 0, N = 1$ energy, the Σ basis set parameters were held fixed at their uncoupled values, and the Π basis set parameters were changed. The parameters for the coupling basis set were significantly different from those which minimized the energy in the uncoupled calculations, requiring six specialized parameters for each state when coupling was considered. The rate of convergence of the coupling terms is illustrated in Figs. 4 and 5 for $H_2{}^+$. The energies converge logarithmically as each sector dimension is increased in turn. To evaluate the contribution of this small off-diagonal term to the energy many fewer basis set elements are needed than for the diagonal terms. The basis set dimensions and nonlinear parameters for states with $N > 0$ are given in Table I. For each symmetry there are two rows. The first row lists the dimensions and parameters for the primary symmetry used for all calculations and the second row lists the quantities for the additional symmetry required for $N > 0$ entering through the coupling of Eq. (13).

The total number of basis functions used can be calculated from the data listed in Table I and is the sum of the values of S defined in Eq. (19) entering for each symmetry. For example,

for H_2^+ Σ_g, $v = 0$, $N = 0$, we used $(13 + 1) \times (5 + 1) \times (13 + 1) = 1176$ functions and for $N = 1$ we used $1176 + (5+1) \times (4+1) \times (6+1) = 1386$ functions. For H_2^+ Π_u, $v = 0$, $N = 1$ we used two runs, each corresponding to one of the rotated basis sets. For the uncoupled set, we had 910 functions, while for the coupled set, we used $910 + 270 = 1180$ functions.

IV. DISCUSSION

Tables II and III compare the present calculations of nonadiabatic energies for H_2^+ and D_2^+ respectively with available precision calculations. In each table the vibration-rotation eigenvalues for the Σ_g symmetry are given first, followed by those for the Σ_u symmetry.

For the Σ_g state the most precise variational basis set calculations are given for H_2^+ in Refs. [34–36,13] and for D_2^+ in Refs. [34,35,13]. Variation-perturbation calculations have been performed by Wolniewicz and Orlikowski [11] for H_2^+ and D_2^+ for all the Σ_g vibration-rotation states but the tabulated results include radiative and relativistic corrections and can not be compared directly with the present work. Using the artificial channel approach Moss carried out extensive nonadiabatic calculations of all the vibrational-rotational states of H_2^+ [13] and D_2^+ [12] for the Σ_g states. His results with radiative and relativistic corrections are in good agreement with Wolniewicz and Orlikowski and he also presented energies without these corrections. In Tables II and III the various calculations for the $v = 0, N = 0$, $v = 0, N = 1$, and $v = 1, N = 0$ states are compared to our calculations. Results listed in Refs. [12,13] are converted from dissociation energies in wavenumbers to atomic units and combined with the asymptotic energy $-M_n/[2(1 + M_n)]$. Our results are consistent with and slightly improve upon the precision of previous calculations.

Only a few high-precision calculations are available for the lowest states of Σ_u symmetry for H_2^+ and D_2^+. Wolniewicz and Orlikowski used the variation-perturbation method and found 3 bound levels for H_2^+ and 7 bound levels for D_2^+ and gave energies of the levels with Σ-Π coupling included. Subsequently, Moss using the artificial channel method including Σ-Π coupling found results in agreement with those of Wolniewicz and Orlikowski for both H_2^+ [13] and D_2^+ [12]. Our Σ_u results are compared with these prior calculations in Tables II and III. For the $v = 0, N = 0$ and $v = 0, N = 1$ states our energies are consistent with the others and of higher precision. However, for the D_2^+ $v = 1, N = 0$ state we found that a quite large basis set ($B = 20, C = 11, D = 36$ with $\alpha = 15.8$, $\beta = 37$ and $\gamma = 2.6$) was required to approach the energies given in Refs. [11,12]. Peek [37] showed that in the Born-Oppenheimer approximation the $v = 1, N = 0$ vibrational wave function can have significant amplitude at values of R as large as several hundred a_0. Our electronic basis set is not explicitly dependent on R and this may account for the large basis size needed. Other methods [10–13] are based on coupled channel approaches that may be better at describing such diffuse vibrational states.

There do not appear to be any published nonadiabatic energies for the lowest electronic state of Π_u symmetry of either H_2^+ or D_2^+. Probably the most accurate study published is that of Bishop *et al.* [38], who investigated the Π_u energies of H_2^+ within the standard adiabatic approximation [7,39]. In Table IV the present nonadiabatic energies are compared to Born-Oppenheimer and standard adiabatic energies. The energy calculated in the Born-Oppenheimer approximation is a lower bound to the true energy while the standard adiabatic and nonadiabatic energies are upper bounds [40,22]. The standard adiabatic energies were

calculated with the diagonal coupling of Ref. [38] rescaled to a proton mass of 1 836.152 701 and the results differ in the seventh decimal place from the values reported in [38]. The present nonadiabatic results lie above the Born-Oppenheimer energy but below the standard adiabatic energy as expected [22].

The energies in Table IV were calculated without the consideration of Eq. (13) leading to one level for each value of N. With the inclusion of the coupling term (13) as described above in Sec. III B our calculations exhibit lambda-doubling in the eigenvalues of Π symmetry. In Table V calculated eigenvalues for the $v = 0$ and 1 states with $N = 1$ are presented for $H_2{}^+$ and $D_2{}^+$. For each value of v the first row gives the energy of the shifted level resulting from the diagonalization of the matrix coupling $|0\rangle$ and $\frac{1}{\sqrt{2}}(|+1\rangle - |-1\rangle)$ and the second row gives the energy of the other, unshifted, level. The energy difference between the two levels is the lambda-doubling.

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TABLES

TABLE I. For $H_2{}^+$ values of the dimensions B, C, and D and the optimized nonlinear parameters α, β, and γ. The values used for $D_2{}^+$ are identical except for the three values listed in parentheses.

		Dimension			Nonlinear parameter		
Type	Symmetry	B	C	D	α	β	γ
I	Σ_g	13	5	13(17)	3.1561	67	37.0
	Π_g	5	4	6	3.0	79	42.0
II	Σ_u	14(10)	11(9)	30	15.8	43	3.1
	Π_u	5	5	11	13.0	97	7.4
III	Π_u	9	6	12(19)	6.0	125	16.5
	Σ_u	8	5	4	5.0	47	3.86

TABLE II. Comparison of nonadiabatic vibration-rotation energies for $H_2{}^+$ for each of the lowest electronic states of Σ_g or Σ_u symmetry. Calculations with $N > 0$ include the coupling term of Eq. (13). Unless indicated otherwise all calculations correspond to a proton mass of 1 836.152 701 in units of the electron mass.

State	Author (Year)	Ref.	Energy
$\Sigma_g, v = 0, N = 0$	Bishop and Cheung (1977)[a]	[34]	−0.597 139 062 5
	Bishop and Solunac (1985)[a]	[35]	−0.597 139 063 18
	Moss (1993)	[13]	−0.597 139 063 1
	Grémaud et al. (1998)	[36]	−0.597 139 063 123(1)
	This work		−0.597 139 063 123 9(5)
$\Sigma_g, v = 0, N = 1$	Moss (1993)	[13]	−0.596 873 738 9
	This work		−0.596 873 738 832 8(5)
$\Sigma_g, v = 1, N = 0$	Bishop and Cheung (1977)[a]	[34]	−0.587 155 675 8
	Moss (1993)	[13]	−0.587 155 679 2
	Grémaud et al. (1998)	[36]	−0.587 155 679 212(1)
	This work		−0.587 155 679 213 6(5)
$\Sigma_u, v = 0, N = 0$	Wolniewicz and Orlikowski (1991)	[11]	−0.499 743 49
	Moss (1993)	[13]	−0.499 743 502 2
	This work		−0.499 743 502 21(1)
$\Sigma_u, v = 0, N = 1$	Wolniewicz and Orlikowski (1991)	[11]	−0.499 739 25
	Moss (1993)	[13]	−0.499 739 268 0
	This work		−0.499 739 267 93(2)[b]

[a]Proton mass 1836.15

[b]For this energy, the basis set had dimension $B = 16$.

TABLE III. Comparison of nonadiabatic vibration-rotation energies for D_2^+ for each of the lowest electronic states of Σ_g or Σ_u symmetry. Calculations with $N > 0$ include the coupling term of Eq. (13). Unless indicated otherwise all calculations correspond to a deuteron mass of 3 670.483 014 in units of the electron mass.

State	Author (Year)	Ref.	Energy
$\Sigma_g, v = 0, N = 0$	Bishop and Cheung (1977)[a]	[34]	−0.598 788 782 0
	Bishop and Solunac (1985)[a]	[35]	−0.598 788 782 22
	Moss (1993)	[12]	−0.598 788 784
	This work		−0.598 788 784 330 8(1)
$\Sigma_g, v = 0, N = 1$	Moss (1993)	[13]	−0.598 654 873 1
	This work		−0.598 654 873 220 5(5)
$\Sigma_g, v = 1, N = 0$	Bishop and Cheung (1977)[a]	[34]	−0.591 603 115 4
	Moss (1993)	[12]	−0.591 603 122
	This work		−0.591 603 121 903 2(1)
$\Sigma_u, v = 0, N = 0$	Wolniewicz and Orlikowski (1991)	[11]	−0.499 888 93
	Moss (1993)	[12]	−0.499 888 937 5
	This work		−0.499 888 937 71(1)
$\Sigma_u, v = 0, N = 1$	Wolniewicz and Orlikowski (1991)	[11]	−0.499 886 38
	Moss (1993)	[12]	−0.499 886 382 5
	This work		−0.499 886 382 63(1)
$\Sigma_u, v = 1, N = 0$	Wolniewicz and Orlikowski (1991)	[11]	−0.499 865 21
	Moss (1993)	[12]	−0.499 865 221 0
	This work		−0.499 865 217 (5)[b]

[a]Deuteron mass 3670.48

[b]For this energy, the basis set had dimensions $B = 20$, $C = 11$, $D = 36$ with nonlinear parameters $\alpha = 15.8$, $\beta = 37$, and $\gamma = 2.6$ as discussed in the text.

TABLE IV. For $H_2{}^+$ the first several eigenvalues of the Π_u symmetry with $N = 1$ calculated nonadiabatically compared with Born-Oppenheimer and standard adiabatic calculations, respectively. For the present calculations, col. 4, the coupling term (13) has not been included.

Vibrational state	Born Oppenheimer	Standard Adiabatic	Present[a]
0	−0.133 905 216 5	−0.133 841 244 8	−0.133 841 939 2
1	−0.132 752 851 6	−0.132 689 153 4	−0.132 689 769 1
2	−0.131 660 981 7	−0.131 597 475 8	−0.131 598 133 6
3	−0.130 631 351 9	−0.130 567 953 2	−0.130 568 676 9
4	−0.129 666 127 2	−0.129 602 748 3	−0.129 603 541 6

[a]Nonlinear parameters $\alpha = 6.0, \beta = 125, \gamma = 16.5$ with $B = 9, C = 6, D = 24$.

TABLE V. Lambda-doubling in nonadiabatic vibration-rotation energies of $H_2{}^+$ and $D_2{}^+$ for the lowest electronic state of Π_u symmetry for $v = 0$ and 1, with $N = 1$. For each value of v the first row gives the energy of the shifted level arising from the coupling term in Eq. (13) and the second row gives the energy of the other, unshifted, level.

Ion	State	Energy
$H_2{}^+$	$\Pi_u, v = 0, N = 1$	−0.133 841 940 395(5)
		−0.133 841 939 176 3(1)
	$\Pi_u, v = 1, N = 1$	−0.132 689 769 820(5)
		−0.132 689 769 121 8(1)
$D_2{}^+$	$\Pi_u, v = 0, N = 1$	−0.134 052 118 044(5)
		−0.134 052 117 739 8(1)
	$\Pi_u, v = 1, N = 1$	−0.133 224 515 520(5)
		−0.133 224 515 448 7(1)

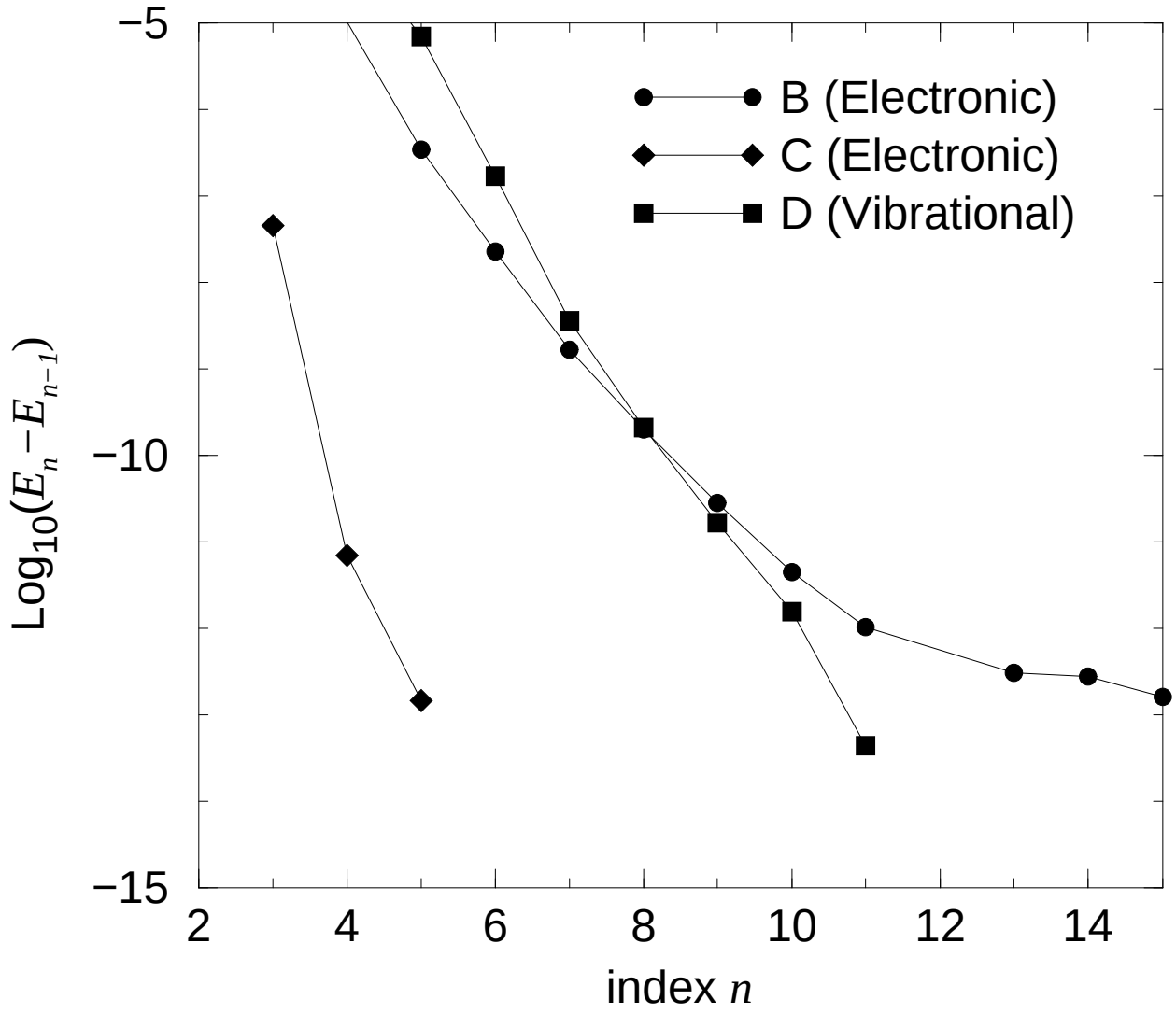

FIG. 1. Convergence study for the ground state Σ_g energy of $H_2{}^+$ with $v = 0, N = 0$. The three basis sectors are fixed at their optimized dimensions for B, C, and D. Then for each sector, in turn, the index of the basis set B, C, or D, is set back to 2 and the value is increased until the optimized value of B, C, or D is reached again. Each line represents the $\log_{10}$ of the energy for the index value n subtracted from the energy for the previous index value. (For sector B we have omitted the energy E_{12}.)

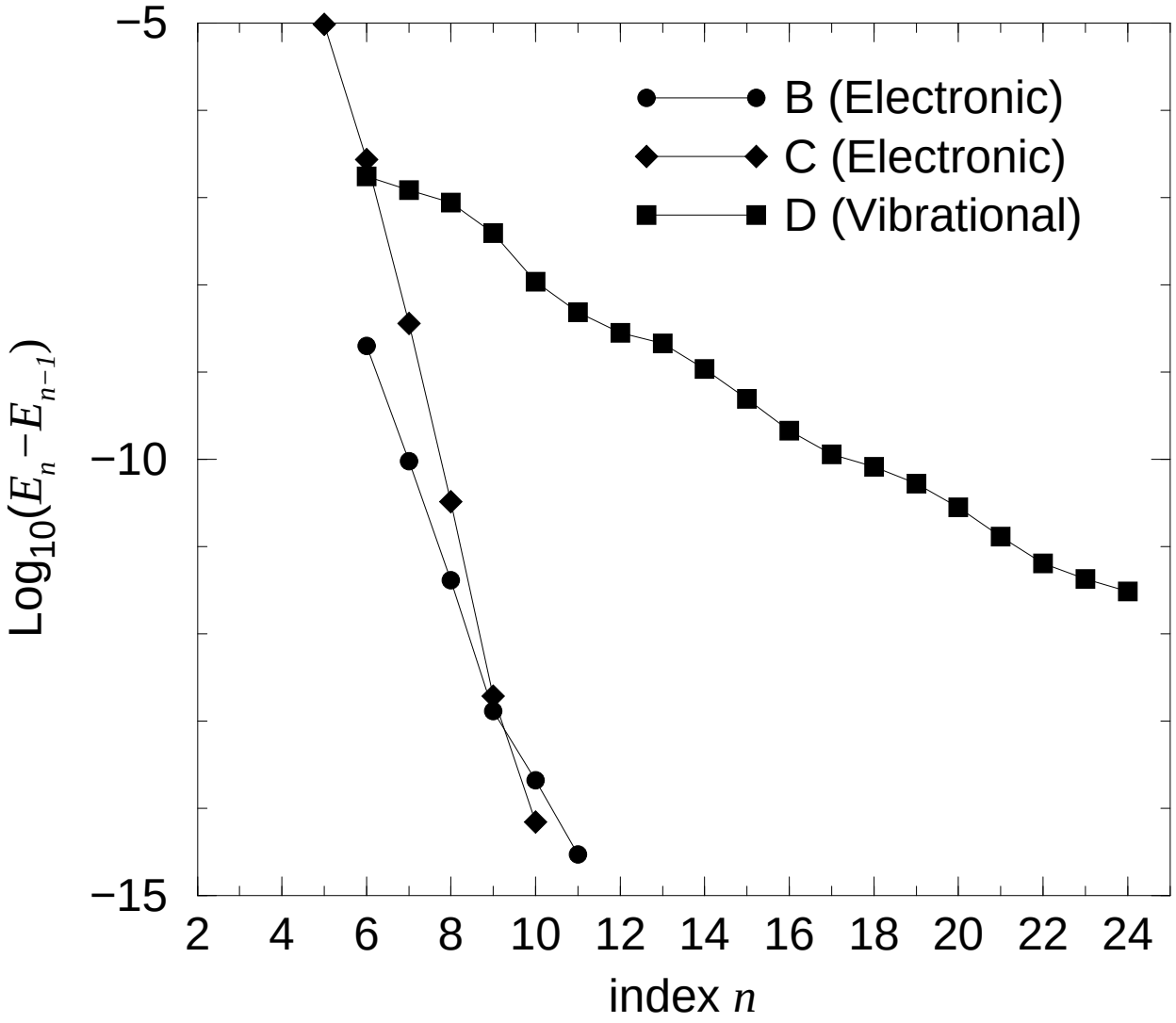

FIG. 2. Convergence study for the Σ_u energy of $H_2{}^+$ with $v = 0, N = 0$.

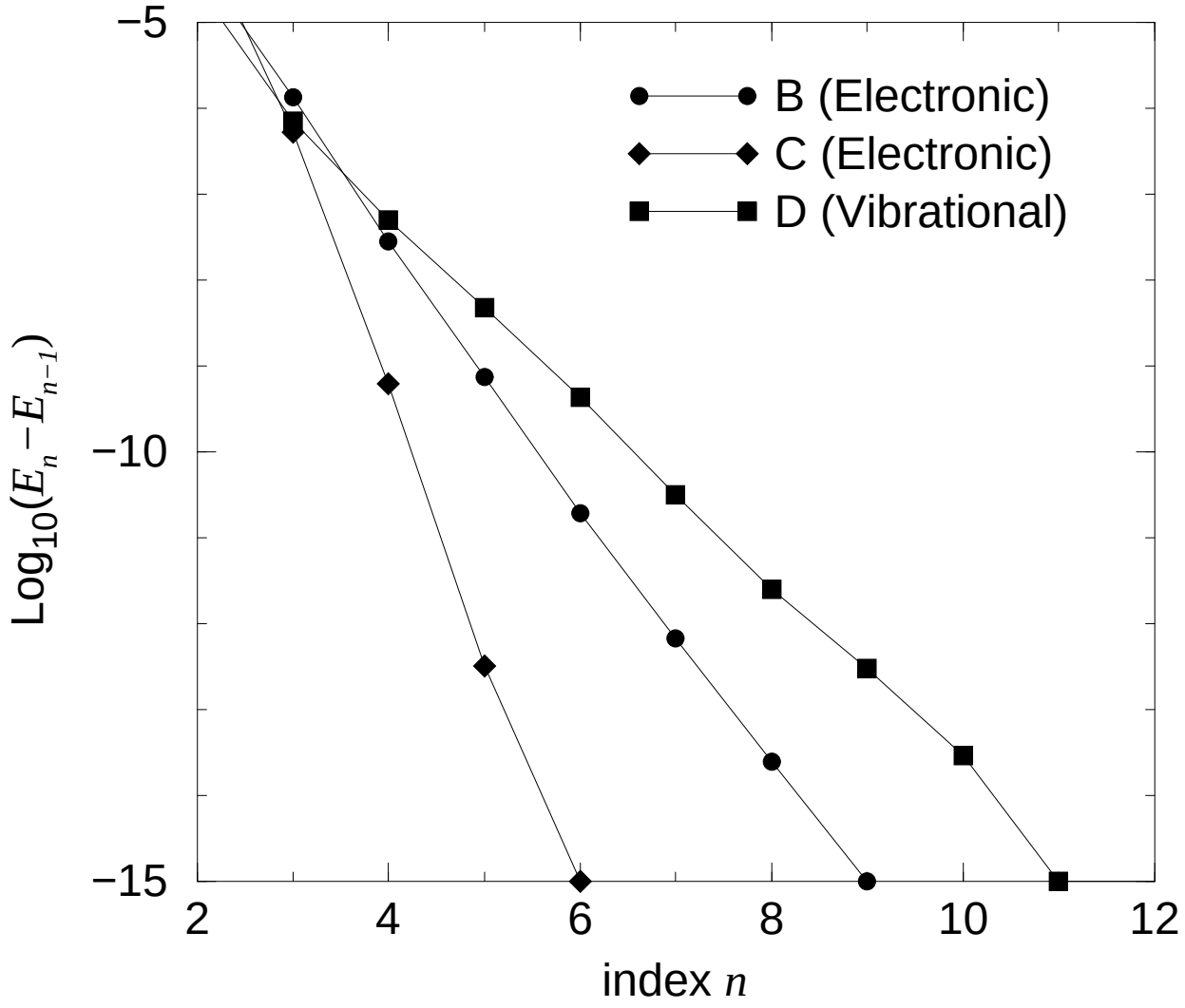

FIG. 3. Convergence study for the Π_u energy of $H_2{}^+$ for the $v = 0, N = 1$ state with with no coupling to the Σ_u symmetry included.

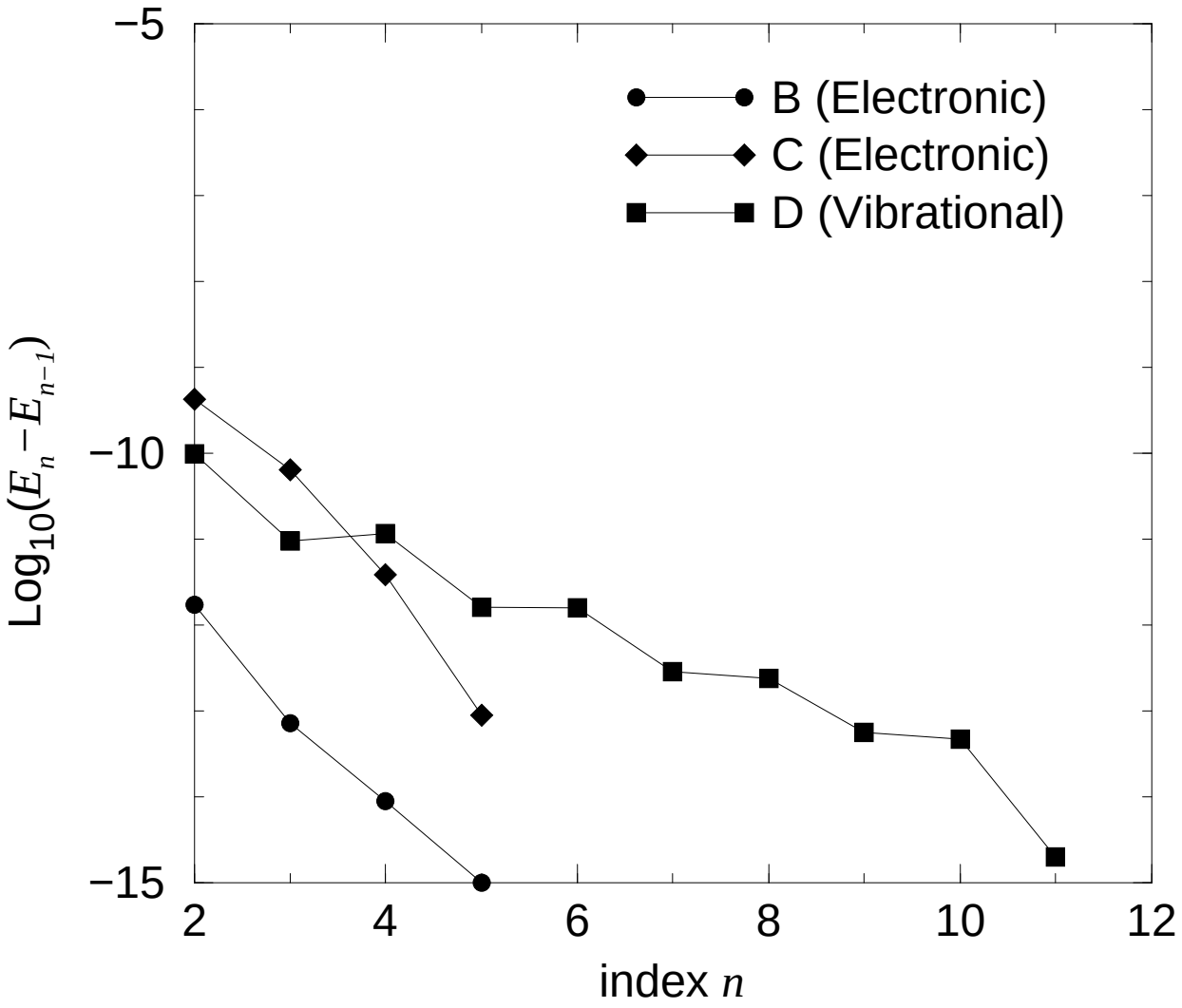

FIG. 4. Convergence study for the energy of $H_2{}^+$ in the Σ_u, $v = 0, N = 1$ state for the basis set of Π_u symmetry entering in the calculation. The Σ_u symmetry basis set is fixed with the optimized size and nonlinear parameters listed in Table I for the calculations of this plot.

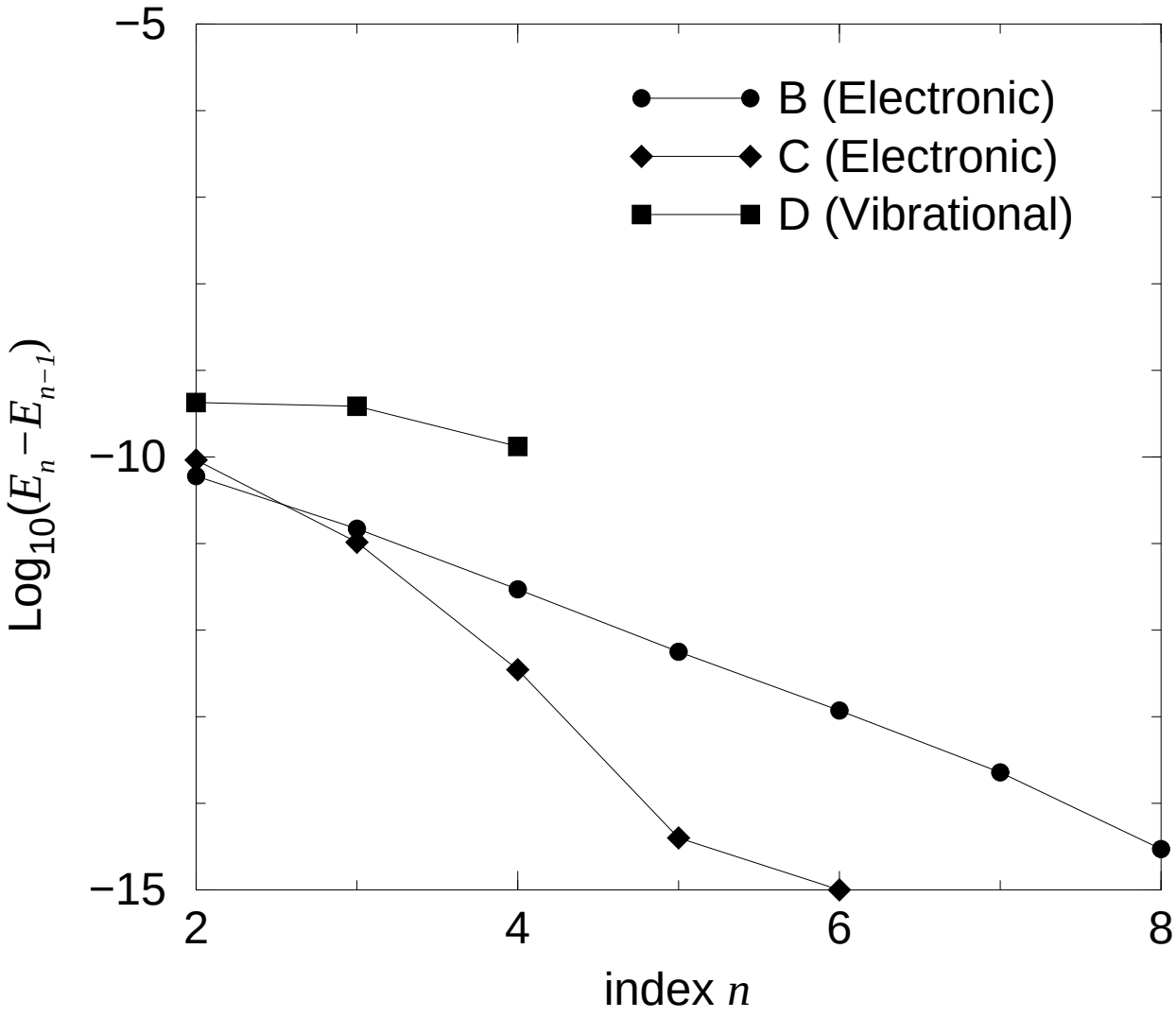

FIG. 5. Convergence study for the energy of $H_2{}^+$ in the Π_u, $v = 0, N = 1$ state for the basis set of Σ_u symmetry entering in the calculation. The Π_u symmetry basis set is fixed with the optimized size and nonlinear parameters listed in Table I for the calculations of this plot.

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